Experimental Section

Melting points are uncorrected. ^1H NMR spectra were recorded at 90 or 400 MHz. Analytical GC was performed using a 2-m × 3-mm glass column packed with Silicone OV-17 on Uniport HP (5%, 60–80 mesh) or a 25-m × 0.25-mm capillary column packed with CBP-10. Column chromatography was performed on silica gel (Wakogel C-200 or C-300). Preparative TLC was carried out on silica gel plates (Wakogel B-5F).

Tri-*n*-butyltin hydride (Bu_3SnH) was synthesized by the reduction of tri-*n*-butyltin chloride (Bu_3SnCl) with $LiAlH_4$. Chlorodi-*n*-butyltin hydride (Bu_2SnClH) was synthesized by the redistribution reaction from di-*n*-butyltin dihydride (Bu_2SnH_2) and di-*n*-butyltin dichloride (Bu_2SnCl_2).[10] Bu_2SnH_2 was obtained by a similar preparation of Bu_3SnH.

α-Alkoxy ketones **1a** and **1d** were synthesized by alcoholysis of the corresponding silyl enol ethers in the presence of iodosobenzene.[13] Benzoin ethers **1b** and **1c** and cyclic compound **1e** were commercially available. α-Siloxy ketone **1f**[14] was prepared by silylation of benzoin with Me_3SiCl–Et_3N.[15]

Representative Procedure for Syn-Selective Reductions Using Bu_3SnH–Bu_4NF. A solution of 0.58 g (2 mmol) of Bu_3SnH in THF (2 mL) was stirred and cooled at 0 °C under N_2. Bu_4NF (2 mmol; 1 M THF solution) and 0.33 g (2 mmol) of **1a** were added. Stirring was continued for 5 h. After quenching with MeOH (5 mL), the solvent was removed under reduced pressure. The residue was subjected to column chromatography with hexane–EtOAc (1:1) to give **2a**[16] as a colorless oil (0.269 g, 81%). Identification of products was performed by ^1H NMR and IR spectroscopy.

Representative Procedure for Anti-Selective Reductions Using Bu_2SnClH. To the solution of 0.24 g (1 mmol) of Bu_2SnH_2 in THF (2 mL) was added 0.31 g (1 mmol) of Bu_2SnCl_2 under N_2. The mixture was stirred at rt for 10 min. The IR band at 1820 cm^{-1} due to the Sn–H bond of Bu_2SnH_2 changed to 1850 cm^{-1}, which indicated the formation of Bu_2SnClH. Ketone **1a** (0.61 g, 2 mmol) was added and this solution was stirred at 0 °C for 5 h. After quenching with MeOH (5 mL), the solvent was removed under reduced pressure. The residue was subjected to column chromatography with hexane–EtOAc (1:1) to give a 1:9 diastereomeric mixture of **2a** and **3a** as a colorless oil (0.239 g, 72%). The isomer ratio was determined by ^1H NMR spectroscopy.

Further purification of diastereomers **2a–e** and **3a–f** was performed by preparative TLC with 4:1 hexane/ethyl ether or Kugelrohr distillation. The relative stereochemistry of diastereomers **2a–e** and **3a–f** was assigned by ^1H NMR comparison with stereochemically defined authentic samples.

***syn*- and *anti*-2-methoxy-1-phenyl-1-propanol (2a and 3a)**: colorless oil[16] purified by Kugelrohr distillation at 105 °C (6 mmHg); IR (neat) 3400, 1080 cm^{-1}; MS *m/z* 166 (M^+); ^1H NMR ($CDCl_3$) **2a** δ 0.98 (d, 3 H, *J* = 6.4 Hz, CH_3), 2.55 (br, 1 H, OH), 3.38 (dd, 1 H, *J* = 6.4 and 7.8 Hz, CHOMe), 3.43 (s, 3 H), 4.40 (d, 1 H, *J* = 7.8 Hz, C*H*OH), 7.25–7.36 (m, 5 H, Ph); **3a** δ 0.98 (d, 3 H, *J* = 6.4 Hz, CH_3), 2.15 (br, 1 H, OH), 3.42 (s, 3 H, OCH_3), 3.54 (m, 1 H, *J* = 6.4 and 3.4 Hz, CHOMe), 4.91 (d, 1 H, *J* = 3.4 Hz, C*H*OH), 7.20–7.40 (m, 5 H, Ph).

***syn*- and *anti*-2-methoxy-1,2-diphenylethanol (2b and 3b)**: mp 84–87 °C (lit.[17] **2a** mp 53 °C; **3a** mp 100 °C); IR (KBr) 3400, 1030, 1045 cm^{-1}; MS *m/z* 228 (M^+); ^1H NMR ($CDCl_3$) **2b** δ 2.45 (br, 1 H, OH), 3.30 (s, 3 H, OCH_3), 4.12 (d, 1 H, *J* = 8.3 Hz, CHOMe), 4.65 (d, 1 H, *J* = 8.3 Hz, C*H*OH), 7.11–7.28 (m, 10 H, Ph); **3b** δ 2.45 (br, 1 H, OH), 3.22 (s, 3 H, OCH_3), 4.34 (d, 1 H, *J* = 5.4 Hz, CHOMe), 4.88 (d, 1 H, *J* = 5.4 Hz, C*H*OH), 7.11–7.28 (m, 10 H, Ph).

***syn*- and *anti*-1,2-diphenyl-2-isopropoxyethanol (2c and 3c)**: mp 63–64 °C; IR (KBr) 3400, 1040 cm^{-1}; MS *m/z* 256 (M^+); ^1H NMR ($CDCl_3$) **2c** δ 1.20 (dd, 3 H, *J* = 6.0 and 8.0 Hz, CH_3), 2.50 (br, 1 H, OH), 3.45–3.65 (m, 1 H, $CHMe_2$), 4.30 (d, 1 H, *J* = 7.5 Hz, CHOPr), 4.65 (d, 1 H, *J* = 7.5 Hz, C*H*OH), 7.00–7.40 (m, 10 H, Ph); **3c** δ 1.03 (dd, 3 H, *J* = 3.0 and 6.0 Hz, CH_3), 2.48 (d, 1 H, *J* = 4.0 Hz, OH), 3.35–3.65 (m, 1 H, $CHMe_2$), 4.50 (d, 1 H, *J* = 5.5 Hz, CHOPr), 4.81 (dd, 1 H, *J* = 4.0 and 5.5 Hz, C*H*OH), 7.13–7.25 (m, 10 H, Ph). Anal. Calcd for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86. Found: C, 79.52; H, 7.84.

***syn*- and *anti*-1-methoxy-1-phenyl-2-propanol (2d and 3d)**: colorless oil;[18] IR (neat) 3400, 1090 cm^{-1}; MS *m/z* 166 (M^+); ^1H NMR ($CDCl_3$) **2d** δ 0.96 (d, 3 H, *J* = 5.9 Hz, CH_3), 1.66 (br, 1 H, OH), 3.24 (s, 3 H, OCH_3), 3.79–3.85 (m, 2 H, CHOMe and C*H*OH), 7.27–7.38 (m, 5 H, Ph); **3d** δ 1.10 (d, 3 H, *J* = 6.3 Hz, CH_3), 1.95 (br, 1 H, OH), 3.30 (s, 3 H, OCH_3), 3.92–3.98 (m, 1 H, C*H*OH), 4.11 (d, 1 H, *J* = 4.9 Hz, CHOMe), 7.27–7.38 (m, 5 H, Ph).

***cis*- and *trans*-2-methoxycyclohexanol (2e and 3e)**: colorless oil[19] purified by Kugelrohr distillation at 55 °C (4 mmHg); IR (neat) 3400, 1080 cm^{-1}; MS *m/z* 130 (M^+); ^1H NMR ($CDCl_3$) **2e** δ 1.20–1.80 (m, 8 H, CH_2), 2.26 (d, 1 H, *J* = 4.4 Hz, OH), 3.25–3.30 (m, 1 H, CHOMe), 3.37 (s, 3 H, OCH_3), 3.82–3.88 (m, 1 H, C*H*OH); **3e** δ 1.20–1.80 (m, 8 H, CH_2), 2.78 (br, 1 H, OH), 2.90–2.98 (m, 1 H, CHOMe), 3.40 (s, 3 H, OCH_3), 3.38–3.45 (m, 1 H, C*H*OH).

***meso*-1,2-Diphenyl-1,2-ethanediol (3f)**. To a solution of 0.24 g (1 mmol) of Bu_2SnH_2 in THF (2 mL) was added 0.31 g (1 mmol) of Bu_2SnCl_2 under N_2. The mixture was stirred at rt for 10 min. Ketone **1f** (0.57 g, 2 mmol) was added and this solution was stirred at 0 °C for 5 h. After quenching with MeOH (5 mL), the solvent was removed under reduced pressure. The residue was subjected to column chromatography with hexane–EtOAc (1:1) to give a desilylated alcohol **3f** (0.385 g, 90%): mp 135 °C (lit.[20] mp 135 °C); IR (KBr) 3350 cm^{-1}; MS *m/z* 214 (M^+); ^1H NMR ($CDCl_3$) δ 2.18 (s, 2 H, 2 OH), 4.84 (s, 2 H, 2 CH), 7.15–7.35 (m, 10 H, Ph).

Acknowledgment. This work was supported by the Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture. Thanks are due to Mrs. Y. Miyaji and Mr. H. Morigichi, Faculty of Engineering, Osaka University, for assistance in obtaining NMR and MS spectra.

Supplementary Material Available: ^1H NMR spectra for compounds **2a–e** and **3a–f** (10 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

(13) Moriarty, R. M.; Prakosh, O.; Duncan, M. P.; Vaid, R. K. *J. Org. Chem.* **1987**, *52*, 150.
(14) **1f**: mp 77–78 °C; IR (KBr) 1680 cm^{-1}; ^1H NMR ($CDCl_3$) δ −0.44 (s, 3 H), 5.67 (s, 1 H), 7.00–7.89 (m, 5 H); HRMS calcd for $C_{17}H_{20}O_2Si$ 284.4301 ($M^{+\cdot}$), found 284.1211.
(15) Corey, E. J.; Snider, B. B. *J. Am. Chem. Soc.* **1972**, *94*, 2549.
(16) Koga, K.; Yamada, S. *Chem. Pharm. Bull.* **1972**, *20*, 526.
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(18) Hassner, A.; Reuss, R. *J. Org. Chem.* **1974**, *39*, 553.
(19) Buck, K. W.; Foster, A. B.; Labib, A.; Webber, J. W. *J. Chem. Soc.* **1964**, 2846. Winstein, S.; Henderson, R. B. *J. Am. Chem. Soc.* **1943**, *65*, 2196.
(20) Clerici, A.; Porta, O. *J. Org. Chem.* **1985**, *50*, 76.

Hydrogenation and Dehydrogenation Reactions of Phenalenones and Dihydrophenalenones

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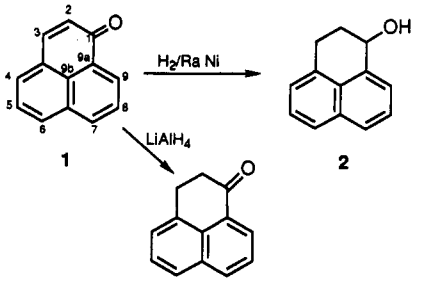
Interest in the phenalene system is due to its interesting chemical properties[1] and also to its potential as a template in drug design.[2a,b] During the course of our studies of phenalenes, 2,3-dihydro-1*H*-phenalenone (**3**) was required as a starting material. Since catalytic hydrogenation has

(1) Darlington, W. H.; Szmuszkovicz, J. *Tetrahedron Lett.* **1988**, *29*, 1883 and references cited therein.
(2) (a) VonVoigtlander, P. F.; Althaus, J. S.; Ochoa, M. C.; Neff, G. L. *Drug Dev. Res.* **1989**, *17*, 71. (b) Tang, A. H.; Franklin, S. R.; Code, R. A.; Althaus, J. S.; VonVoigtlander, P. F.; Darlington, W. H.; Szmuszkovicz, J. *Drug Dev. Res.* **1990**, *21*, 53.

0022-3263/92/1957-4051$03.00/0

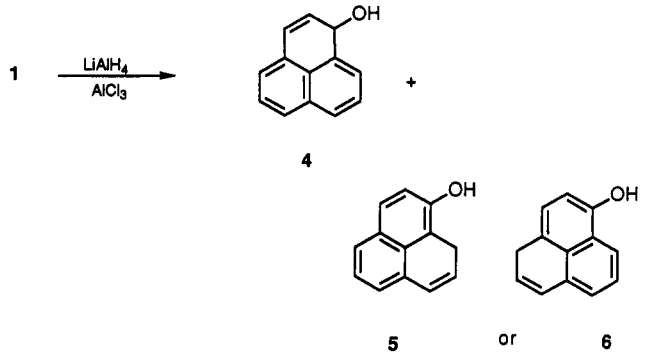
often been used to convert enones to saturated ketones, we turned to this reaction to convert the commercially available 1*H*-phenalenone (perinaphthenone) (1) to 3.



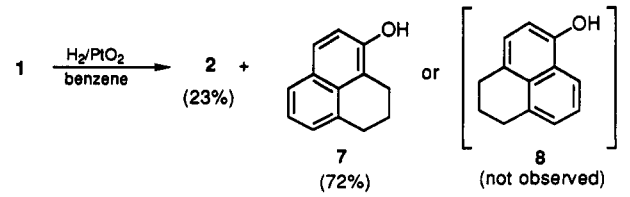
1 2 3

The reduction of 1 was first examined by Fieser and Newton[3] who were interested in obtaining 2,3-dihydro-1*H*-phenalen-1-ol (2). Catalytic hydrogenation in the presence of Raney nickel succeeded only when aged catalyst was used; more active catalyst yielded "considerable quantities of phenolic material"; the exact nature of this material was not established. Boekelheide and Larrabee[4] later examined the reduction of 1 with lithium aluminum hydride and found that the principal product was 2,3-dihydro-1*H*-phenalenone (3) which was accompanied by small amounts of 1*H*-phenalene (1*H*-perinaphthene) and unidentified phenolic material.

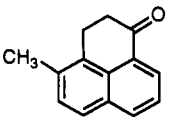
Later in a somewhat related study of the reduction of 1 with aluminum hydrides, it was reported[5] that both carbonyl and conjugate reduction occurred to produce compounds 4 and 5, respectively. The alternative phenolic compound 6 was not considered but also not explicitly excluded.



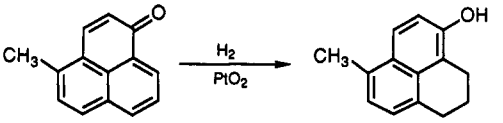
Hydrogenation of 1[6] in a Parr apparatus over Adams' catalyst in benzene gave, in addition to alcohol 2 as a minor product, only a phenolic product whose spectroscopic properties were in accord with structure 7 or 8.



In order to distinguish the two aromatic rings of 1 from each other, an analog of 1, 4-methyl-1*H*-phenalenone (10), was prepared by Pd-catalyzed dehydrogenation of 9 and subjected to the same hydrogenation conditions. The phenolic product was identified as 7-methyl-2,3-dihydro-



9

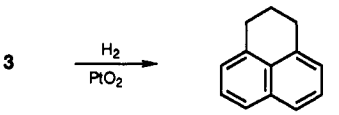


10 11

1*H*-phenalen-4-ol (11) since its ^1H NMR spectrum exhibits a signal at δ 2.6 for the methyl group (cf. δ 2.7 in 10), consistent with its attachment to an aromatic rather than a saturated ring. The rest of its spectrum strongly resembles that of 7. Therefore, it can be concluded that the hydrogenation products of both ketones result in β-naphthol derivatives, as proposed for the hydride reduction of 1.[5]

The exact sequence of reduction events is difficult to determine. In analogy with the hydride reduction proposal,[5] one might envision formation of 5 by 1,12 conjugate addition followed by further reduction of the alkene double bond to finally yield 7. Isomerization over the catalyst of the enol of ketone 3, formed by 1,4-reduction of 1, cannot be excluded, but no reaction was observed when ketone 3 was treated with Adams' catalyst in acetic acid.

That compound 2 did not arise from overreduction of the desired ketone 3 was shown by the conversion of 3 to 2,3-dihydro-1*H*-phenalene[7a,b] under the identical reduction conditions (PtO_2, H_2). This result also suggests that allylic alcohol 4 and not 3 is the immediate precursor of alcohol 2 in the reduction of ketone 1.



The preparation of ketone 10 from 9 by dehydrogenation with Pearlman's reagent suggested that this method might be generally applicable to the preparation of enones. The parent phenalenone 1 was similarily prepared from ketone 3, and *trans*-4-phenyl-3-buten-2-one was obtained in 50% conversion in toluene from 4-phenylbutan-2-one along with an equimolar amount of benzyl acetate.[8] However, no dehydrogenation was observed with propiophenone, indanone, α-tetralone, or cyclohexanone.

Experimental Section

Solutions were generally concentrated by using a Büchi rotary evaporator at 15–20 Torr after being dried ($MgSO_4$ or Na_2SO_4) and filtered. Crude products were generally purified by recrystallization or by column chromatography. All reagents were obtained commercially from Aldrich Chemical Co., Inc. unless otherwise stated. ^1H NMR spectra were obtained at 300 MHz and ^{13}C NMR spectra were obtained at 75 MHz with $CDCl_3$ as a solvent unless otherwise stated. Melting points were determined with a Thomas Hoover Unimelt apparatus and are not corrected.

General Procedure of Hydrogenation Reactions of Phenalenones: 2,3-Dihydrophenalen-1-ol (2) and 2,3-Dihydrophenalen-4-ol (7). Into the Parr hydrogenation flask was added 1*H*-phenalenone (1) (119 mg, 0.66 mmol), platinum oxide (25 mg),

(3) Fieser, L. F.; Newton, R. *J. Am. Chem. Soc.* **1942**, *64*, 917.
(4) Boekelheide, V.; Larrabee, C. E. *J. Am. Chem. Soc.* **1950**, *72*, 1245.
(5) Pagni, R. M.; Watson, C. R., Jr. *Tetrahedron* **1973**, *29*, 3807.
(6) Fieser, L. F.; Gates, M. D., Jr. *J. Am. Chem. Soc.* **1940**, *62*, 2335.
(7) (a) Simpson and Daub (Simpson, J. E.; Daub, G. H. *J. Org. Chem.* **1979**, *44*, 1340) converted 3 to 2,3-dihydro-1*H*-phenalene with LAH/$AlCl_3$. (b) A similar reduction using Pd/C in acetic acid has been reported: Heidelberger C.; Rieke, H. S. *Cancer Res.* **1951**, *11*, 640.
(8) Palladium(II) acetate has long been known as the catalyst for acetoxylation of toluene. Bryant, D. R.; McKeon, J. E.; Ream, B. C. *J. Org. Chem.* **1968**, *33*, 4123.

and benzene (10 mL). The mixture was subjected to hydrogenation for 7 h, and then it was filtered and concentrated. The crude product was separated by column chromatography on silica gel (hexanes/ethyl acetate = 10/1) to give 2[9] as a colorless solid (28 mg, 23%) and a mixture of two components (ratio = 6:1) as a colorless solid (88 mg, 72%). A pure sample of the major component was obtained from repetitive chromatography[10] of the mixture; it was characterized as 7: mp 107-108 °C (recrystallized from hexane/ether); ^{1}H NMR (200 MHz) δ 7.58 (δ, J = 8.8 Hz, 2 H), 7.21 (m, 2 H), 7.04 (d, J = 8.9 Hz, 1 H), 4.86 (s, 1 H), 3.05 (t, J = 6.0 Hz, 2 H), 2.95 (t, J = 6.4 Hz, 2 H), 2.06 (quin, J = 6.1 Hz, 2 H); ^{13}C NMR δ 148.81, 134.93, 130.98, 129.10, 126.94, 125.88, 124.31, 123.11, 117.15, 117.10, 30.73, 23.56, 22.12; MS (EI), m/e (rel intensity) 184 (100, M$^+$), 183 (32), 181 (8), 169 (11), 167 (8), 165 (19), 152 (11), 82 (11), 76 (8); HRMS m/e calcd for $C_{13}H_{12}O$ 184.0888, found 184.0893.

7-Methyl-2,3-dihydrophenalen-4-ol (11). Hydrogenation of 120 mg of phenalenone 10 (vide infra) gave 76 mg of 11 as a yellow solid: mp 149-150 °C (recrystallized from Skelly F/ether):[11] ^{1}H NMR δ 7.75 (d, J = 9.0 Hz, 1 H), 7.08 (m, 3 H), 4.95 (m, 1 H), 3.02 (t, J = 6.2 Hz, 2 H), 2.97 (t, J = 6.2 Hz, 2 H), 2.61 (d, J = 0.6 Hz, 3 H), 2.05 (m, 2 H); ^{13}C NMR δ 148.76, 133.10, 132.05, 131.08, 128.17, 124.13, 123.89, 123.26, 117.77, 116.59, 30.78, 23.77, 22.28, 19.41; MS (EI) m/e (rel intensity) 198 (100, M$^+$), 183 (55), 165 (30), 152 (11), 82 (25); HRMS m/e calcd for $C_{14}H_{14}O$ 198.1045, found 198.1053.

2,3-Dihydro-1*H*-phenalene was obtained as a solid, mp 82-84 °C, in 87% yield from ketone 3: ^{1}H NMR[12] (CCl_4) δ 7.53 (d, J = 8.1 Hz), 7.24 (t, J = 7.1 Hz), 7.09 (d, J = 6.8 Hz), 3.06 (t, J = 5.9 Hz, 4 H), 2.06 (quin, J = 5.8 Hz, 2 H); ^{13}C NMR[13] (CCl_4) δ 135.34, 133.49, 129.85, 125.60, 124.76, 123.30, 31.10, 22.88; MS (EI) m/e (rel intensity) 168 (100, M$^+$), 167 (59), 165 (40), 153 (46), 152 (30), 144 (24), 129 (15), 83 (27), 82 (22).

General Procedure of Dehydrogenation Reactions of 2,3-Dihydro-1*H*-phenalenones. The bomb was loaded with $Pd(OH)_2$ on carbon (402 mg), phenalenone 3 (57 mg, 0.31 mmol), acetic acid (0.5 mL), and benzene (5 mL). The mixture was heated at 100 °C for 40 h and then was filtered through a pack of silica gel and Na_2CO_3. The filtrate was concentrated in vacuo to give 1*H*-phenalenone (1) (available from Aldrich Chemical Co., Inc. as perinaphthenone) as a yellow crystalline solid, mp 153-155 °C (35 mg, 61%): ^{1}H NMR δ 8.62 (dd, J = 7.4, 1.2 Hz), 8.18 (dd, J = 8.1, 1.1 Hz), 8.02 (d, J = 8.2 Hz), 7.74 (m, 3 H), 7.58 (dd, J = 8.2, 7.1 Hz), 6.74 (d, J = 9.8 Hz); ^{13}C NMR δ 185.79, 141.92, 134.99, 132.07, 131.99, 131.47, 130.48, 129.33, 129.06, 127.71, 127.43, 127.07, 126.60. (The ^{1}H NMR spectrum matches that reported by the Aldrich Chemical Co., Inc.).[14]

4-Methyl-1*H*-phenalenone (10) was obtained as a yellow solid starting from compound 9:[15] yield 354 mg (79%); mp 98-99 °C (recrystallized from EtOAc);[11] ^{1}H NMR δ 8.62 (dd, J = 7.4, 1.3 Hz), 8.13 (dd, J = 8.0, 1.1 Hz), 8.05 (d, J = 10.1 Hz), 7.90 (d, J = 8.4 Hz), 7.70 (t, J = 7.7 Hz), 7.41 (d, J = 8.4 Hz), 6.73 (d, J = 10.1 Hz), 2.73 (s, CH_3); ^{13}C NMR δ 185.51, 140.82, 137.79, 134.97, 131.92, 131.13, 130.60, 130.10, 129.27, 128.46, 127.97, 126.18, 125.00, 19.29; MS (EI) m/e (rel intensity) 194 (85, M$^+$), 165 (100), 139 (12), 82 (26), 52 (13); HRMS m/e calcd for $C_{14}H_{10}O$ 194.0732, found 194.0735.

Acknowledgment. We thank the Upjohn Company for supporting this research.

Supplementary Material Available: ^{1}H and ^{13}C NMR for compounds 7, 10, and 11 (6 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and may be ordered from the ACS; see any current masthead page for ordering information.

(9) The ^{1}H NMR spectrum of this compound is identical to that of the authentic compound obtained from the reduction of 3 with LAH/$AlCl_3$.[7a]

(10) The minor component was obtained in impure form. HRMS indicates a molecular formula of $C_{26}H_{22}O_2$.

(11) Duplicate elemental analyses did not produce satisfactory results.

(12) Shannan, R. L.; Cox, R. H. *Tetrahedron Lett.* **1973**, 1603.

(13) Hunter, D. H.; Stothers, J. B. *Can. J. Chem.* **1973**, *51*, 2884.

(14) Pouchert, C. *The Aldrich Library of NMR Spectra*, 2nd ed.; Aldrich Chemical Co.: Milwaukee, 1983; Vol. 2 p 80(B).

(15) Klyne, W.; Robinson, R. *J. Chem. Soc.* **1938**, 1991.

Practical Synthesis of BINAP-Ruthenium(II) Dicarboxylate Complexes

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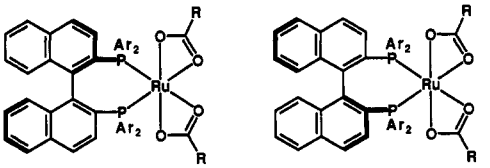
BINAP-Ru(II) dicarboxylate complexes of type 1 serve as excellent catalyst precursors for highly enantioselective hydrogenation of a wide range of prochiral functionalized olefins.[1] The stereoselective hydrogenation allows efficient asymmetric synthesis of terpenes,[2] amino acids,[3] isoquinoline alkaloids including morphines,[4] carbapenem antibiotics,[5] prostaglandins,[6] anti-inflammatory naproxen,[7] etc. This paper discloses a convenient procedure for the preparation of the significant Ru complexes using commercially available BINAP[8] and a Ru complex. This method is high-yielding and much simpler than our original procedure.[9,10]



Δ-(*R*)-1 Λ-(*S*)-1

a, Ar = C_6H_5; R = CH_3
b, Ar = C_6H_5; R = C_6H_5
c, Ar = 3,5-$(CH_3)_2C_6H_3$; R = CH_3

The present synthesis starting with $[RuCl_2(benzene)]_2$ consists of a high-temperature ligand exchange between benzene and optically pure BINAP[10] followed by displacement of the chlorides with carboxylates. Thus, when a mixture of $[RuCl_2(benzene)]_2$[11] and (*R*)- or (*S*)-BINAP (Ru:BINAP = 1.05:1) was heated in *N*,*N*-dimethylformamide (DMF) at 100 °C for 10 min, the exchange of the neutral ligands occurred facilely to give BINAP-$RuCl_2$ complexes. The chloride ligands were then displaced by acetates by treatment of the DMF solution with 20-fold excess of sodium acetates in methanol at room temperature

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